Tutorial 3.5 – Solvent Extraction

Slide 1. Solvent Extraction

This tutorial describes the process of solvent extraction as it is used in the analysis of several different radionuclides.

Slide 2. Learning Objectives

When this module is completed you should be able to:

- List the 5 steps involved in a typical solvent extraction protocol.
- Define the term "hydration layer."
- Explain how complexation ligands promote the migration of ions into non-polar solvents.
- Calculate the volumes and number of re-extractions required to extract a given fraction of a radionuclide based on its distribution ratio.
- Discuss the similarities and differences between traditional solvent extraction and solid-phase solvent extraction.

The key concepts identified in this tutorial are:

- Solvent extraction involves many different basic chemical principles.
- The charge density of a radionuclide and its hydration sphere will be lowered when ligands are used that can complex with the radionuclide being determined. The lowering of the charge density allows for extraction into non-polar solvents.
- The separation of the radionuclide of interest and contaminants, both radioactive and stable, can be achieved by selective chemical conditions creating differences in solubility.

Slide 3. What is Solvent Extraction?

Solvent extraction is a process whereby two immiscible liquids are vigorously shaken in an attempt to disperse one in the other so that solutes can migrate from one solvent to the other. The picture on the right shows the shape of a traditional separatory funnel. When the two liquids are *not shaken* the solvent to solvent interface area is limited to the geometric area of the circle separating the two solvents. However as the two liquids are vigorously shaken the solvents become intimately dispersed in each other.

- The dispersal is in the form of droplets.
- The more vigorous the shaking the smaller the droplets will be.
- The smaller the droplets are the more surface area there is between the two solvents.
- The more surface area between the two solvents, the smaller the linear distance will be that molecules will have travel to reach the other solvent and migrate into it.
- The shorter the linear distance traveled by the molecules the more rapid will be the extraction.

Why do the molecules migrate from one phase into another? The fundamental reason is solubility. The molecules will preferentially migrate to the solvent where they have the greatest solubility. If the molecules are very polar they will generally favor the aqueous phase. If the molecules are non-polar they will favor the organic phase.

The key concept to take away at this point is that the process of solvent extraction requires that the chemist adjust the solution conditions so that the radionuclide of interest is in the proper oxidation state and the solution pH is adjusted so that the appropriate complexing agent will form a neutral complex that will easily migrate into the organic phase based on those chemical conditions

Slide 4. The Solvent Extraction Process

There are five general steps that are involved in the solvent extraction process. They rely on the fact that the solution conditions have been optimized to maximize the extraction for one radionuclide over the others:

1. The first step is to ensure that the proper complexing agents have been added to the aqueous phase so that the extractable complex is of sufficiently low charge density, so that the transfer of the radionuclide to the organic phase will be maximized.
2. In the second step, the equilibration process occurs by shaking of the separatory funnel. Unless otherwise specifically noted in a particular method, the amount of time that the two phases are shaken during this step is about 2 minutes. The initial organic phase is separated and set aside.
3. Step three involves a process known as re-extraction. The original aqueous phase is extracted with a fresh aliquant of the organic phase of the same volume as the first. This improves the efficiency of extraction of the radionuclide of interest. After step two is repeated the two organic phases are combined. The aqueous phases are discarded at this point unless they are needed for analysis of radionuclides not extracted.
4. In step four the combined organic phases are equilibrated with a solution of aqueous phase that is of the same composition as the original sample solution, but without any sample. This step helps to ensure that any interfering materials that may have been extracted are re-distributed back to the aqueous phase, while the radionuclide of interest remains in the organic phase. This phase known as *the wash* is then discarded.
5. The final step is to strip the radionuclide of interest back into an aqueous phase using a pH and lower concentration of complexing agent so that migration back to the aqueous phase is favorable.

Slide 5. Hydration and Charge Density

Any ion in an aqueous solution is solvated by water molecules that form a sphere around the ion. Note that in the picture to the right that the oxygen atoms of the water molecules are facing the central metal ion. Since the charge on the overall ion plus its hydration sphere is still the same as the charge on the metal ion, the *charge density* or charge per unit volume, is reduced.

Slide 6. Solvent Extraction and Charge density

The migration of the radionuclide into the organic phase occurs after the complexation process has occurred. The ligands that replace the primary hydration sphere further reduce the ion charge density allowing the solvation sphere to be changed from water to the solvent at the interface of the two phases.

The diagram on the right is of two different organic molecules that are used as extracting agents for different radionuclides. In each case the ligand has an ionic counter ion charge and a non-polar aspect to its structure that aids in the overall reduction in charge.

Slide 7. Complexation Ligands or Chelating Agents

Chelating agents all have the property of being able to share electrons with vacant atomic orbitals of a central metal ion. These chelating agents act like a Lewis Base, which is any material that has at least one unshared pair of electrons. Chelating agents will therefore usually contain heteroatoms (oxygen, nitrogen, sulfur, or halogens).

Listed on the slide are some of the chelating agents that are used in specific analytical methods for radionuclides.

Slide 8. Example of a Specific Chelating Agent—Trioctyl Phosphine Oxide

Trioctyl phosphine oxide, also called TOPO, contains a strong dipole moment centered on the phosphorus-oxygen bond. The oxygen being more electronegative is the end that will provide the unshared pair of electrons for bonding with the vacant orbitals of a metal ion. The long side chains of this molecule help to increase the size of the complexed metal ion, thus decreasing the charge density and making it appear closer to *zero* charge. This hydrophobic end also aids in the dissolution in organic solvents. TOPO is used in the extraction of uranium as shown in this Module on Slide 16.

Slide 9. Organic Solvents

The table on this slide identifies various organic solvents based on their elemental characteristics. Some solvents are also chelating agents as noted on the chart. The phosphate based compounds TOPO and TBP are liquids at room temperature and can be both solvents and complexing agents, while the sulfur based compounds thenoyl trifluoro acetylacetone (TTA) and diphenylthiocarbazone (dithizone) are solids and 2,3 dimercaptopropanol (called British Anti-Lewisite, or BAL) is an oily liquid. These sulfur based compounds are only used in combination with solvents.

Slide 10. Choice of Solvent System

Most methods that use solvent extraction have used a trial and error approach. The exact nature of the complexes formed and the conditions for their formation and extraction are not nearly as important as the fact that certain combinations of solvents and chelating agents provide the largest differences in the extractability of one radionuclide over another.

This slide represents pictorially what we have described as the five step solvent extraction process. The key to a successful extraction is that the analyte and the interferent have extractability factors that are at least a factor of 100 different. Keep in mind that the interferent may be a radionuclide or other material (non-radioactive) that hinders the analysis of the radionuclide of interest.

Slide 11. Extraction and Re-Extraction

The extractability of a radionuclide is defined by a factor called the distribution ratio, D_R. The key concept for the overall separation of a radionuclide from any interferents is that their solubilities in the two phases should be sufficiently different to effect a separation in a reasonable volume and an initial plus re-extraction process. This means that their D_R values will be significantly different by a factor of at least 100.

Slide 12. The Distribution Ratio

The equation shown on the right defines the distribution ratio. It is easy to remember because most of the solvents we use are less dense than water and so they float on top. In the equation the ratio is defined by the concentration in both phases *after one* equilibration. The distribution ratio is simply a mass transfer effect is been empirically determined. Values of D_R can range from less than one to greater than 10,000.

During an initial extraction we would want to use solution conditions that favor a D_R for the radionuclide of interest of at least 100. This would mean that greater than 99% of the radionuclide would end up in the organic phase. Performing a second extraction with fresh organic phase on the sample solution, and then combining the two organic phases would provide greater than 99.99% removal of the radionuclide of interest from the aqueous phase.

Slide 13. Calculating Volumes and Extractions

How does one select the correct volume to perform an extraction? If we select an amount to remain in the aqueous phase that we deem acceptable, let's say 0.01%, we can determine the combination of number of extractions needed and organic phase volume to effect this using the equation on the right. In this equation, X represents the mass of analyte initially present in the aqueous phase, X-sub-n represents the mass of analyte remaining in the aqueous phase after n extractions. This equation applies when the volume of organic extractant V_{org} is the same each time a successive extraction of the original solution is performed.

You will find that one of the results of using this equation is that you can maximize the amount of radionuclide extracted by performing multiple extractions with small volumes rather than performing one extraction with a single larger organic volume.

Slide 14. Test yourself Exercise #1. Extraction Calculation

Using the equation from the previous slide, calculate *n* the number of extractions required to achieve an extraction of uranium into the heptane phase equivalent to 99%. [Hint: Remember to convert percentage to a fraction.]

Slide 15. Test Yourself Exercise #1 Solution

The solution to problems like these frequently results in a fractional answer. However we can't perform a fraction of an extraction. Thus in order to achieve *at least* the desired percent extraction, you need to take the answer obtained and round to the next highest integer.

Slide 16. Washing and Stripping.

Once we have the radionuclide of interest in the combined organic phases, we want to ensure that we have removed as much of the interfering materials as possible. The next step is referred to as washing, because we equilibrate the organic phase with an aqueous phase that is isotonic to the original sample aqueous phase—except there are no radionuclides or other interferents present. This washing phase helps to eliminate any of the interfering species from the organic phase.

Following the washing phase is the stripping phase. This phase involves equilibrating the organic phase containing the radionuclide of interest with an aqueous phase that will break up the

organic phase complex so that the radionuclide will re-distribute back to the aqueous phase. Usually the aqueous phase has a significantly different pH than the original extracting solution, and it has none of the complexing agent. Stripping is generally performed as one step, and it usually ensures an overall reduction in volume.

Slide 17. Separation and Analysis of Uranium per EPA Method 907.
A general outline of the EPA method for uranium separation is identified on this slide. As you can see this not only involves solvent extraction but co-precipitation, and complexation. In the original method gas proportional counting was used and total uranium only could be reported. However, alpha spectrometry does allow the user to speciate the uranium isotopes and quantitate them separately.

Slide 18. Review of Part I
The technique of solvent extraction has been used for a long time and it is very effective at separating radionuclides form interfering ions. The process is based on the formation of a low charge density or neutral complex that will have a higher solubility in the organic solvent than it does in water. When the two solvents are adequately mixed, the complexed ion will migrate to the phase where it has the higher solubility. The empirical function that identifies the extent of this migration is called the distribution ratio.

The drawbacks to solvent extraction are that it is a labor intensive process and it generates organic solvents as wastes that are usually hazardous waste. In the next slides we will discuss new technique that avoids the use of organic solvents by coating a neutral resin bead with a thin film of an organic compound that is not hazardous. This technique is known as *Stationary Phase Solvent Extraction.*

Slide 19. Stationary Phase Solvent Extraction
Stationary phase Solvent Extraction is a process by which an organic chelating agent is sorbed onto the surfaces of an inert ion exchange resin bead as a very thin film. The organic compound is a high boiling point liquid or potentially a solid material that has an extremely low solubility in water or acid solution. The application of the organic compound as a thin film throughout the resin bead allows a tremendous increase in the surface contact area between the aqueous phase and the organic phase. It is far more effective than trying to force two immiscible liquids into tiny droplets by mechanical shaking.

The compounds used for this process are better suited to complexing with the actinides based on the geometry of the f-orbitals of the transuranics. This means that separation from non-radioactive ions is facilitated at the same time as separating out the radionuclides of interest by differential solubility in the organic phase. So by passing an aqueous phase over a SPSE column you have a continuous solvent extraction process.

Slide 20. Function of SPSE Resins.
The organic molecules used for SPSE usually have a significant viscosity. In order to uniformly coat the resin bead and all the internal channels a solvent of lower density and viscosity is used to dissolve the organic material and then equilibrate the resin with that solution. After draining

off the solvent the resin is flushed with water, in which the organic material has basically zero solubility.

Slide 21. Modified Distribution Ratio: The Capacity Factor *k′*

Since the process of SPSE is different from traditional solvent extraction, a different type of constant associated with a particular organic compound called the capacity factor or *k′* value is used. Just like in solvent extraction or ion exchange the larger the value of the capacity factor the better will be the migration of the ion to the organic phase. Additionally the bigger the *difference* in capacity factor for two ions the better will be their separation on a SPSE column. Thus as the liquid eluent flows through the column, different ions will be eluted based on the solvent volume and their individual *k′* factor with the concentration of eluent.

The process lends itself to batch analysis of samples since the columns can be set up and eluted simultaneously.

Slide 22. UTEVA Extractant Resin

One of the first SPSE products that were manufactured was U/TEVA (where TEVA is an acronym for tetravalent actinide). This particular organic material, diamyl amyl phosphonate has a particularly strong affinity or capacity factor for tetravalent actinides. The only exception is that uranium six is also strongly retained by this column.

Slide 23. Example of Actinides Separation on U/TEVA Resin

The two graphs on the right show the capacity factor of this resin as a function of nitric acid or hydrochloric acid concentration. These factors are empirically determined. The americium as a +3 ion is not appreciably retained on this resin and effectively washes through while thorium and U (VI) are retained. Note that for nitric acid solutions that uranium (VI) and thorium are virtually identical in capacity factor. However, if we switch the aqueous phase to 3 M hydrochloric acid the separation of capacity factors is about a factor of 100. This difference in capacity factor allows effective separation of these two radionuclides.

Slide 24. Transuranic Resin Extractant Molecule

The extractant molecule shown here, cetylphenyl-N,N-di-isobutyl carbamoylphosphine oxide [CMPO], is of general value in allowing separation of different transuranic ions from each other.

Slide 25. Example of Actinide Separation using TRU Resin

Here again the graph shows the change in capacity factor as a function of nitric acid concentration for four different ions. Note that the values for iron and calcium are generally much lower than for that of uranium and plutonium. Thus for water samples containing iron and calcium at ppm concentrations, they will easily pass through the resin column at a concentration of ~0.5 M nitric acid while any plutonium or uranium is exchanged. The plutonium and uranium may then be eluted by dropping the acid concentration to 0.01 M.

For all of these curves of *k′* versus eluent concentration it is important to see that the oxidation state of each ion is clearly identified. This is important as the k’ value will be different for different oxidation states.

Slide 26. Effects of Other Ions on SPSE

The effect that high or low acid concentrations have on capacity factors can also be modified by addition of other complexing agents. In this example the concentration of hydrochloric acid is held constant at 1 M while the concentration of oxalic acid is increased. The k' value for neptunium(IV) falls off much more sharply then does that of U(VI). Thus at concentration of 0.01 M oxalic acid effective separation of uranium from neptunium can be achieved. Here again the oxidation state of the transuranic is important.

Slide 27. Advantages of SPSE and Solvent Extraction

The advantages of both types of chemical separation are shown in this table.

Slide 28. Disadvantages of SPSE and Solvent Extraction

One of the most significant disadvantages of SPSE for drinking water analyses is that these materials are not part of any EPA approved method. Therefore they cannot be used for drinking water analysis under 40 CFR. However this will be changing in the near future.

Slide 29. Conclusion

This concludes our module on Solvent extraction. You should be able to:

- Describe the five steps in the solvent extraction process and the reason for each step.
- Calculate how many extraction steps will be needed to remove a given fraction of radionuclide from an aqueous phase.
- Describe the importance of mechanical agitation in the solvent extraction process.
- Describe the similarities between solvent extraction and stationary phase solvent extraction.